(19) Europäisch s Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 469 690 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **91202673.9**

(51) Int. Cl.5: **A01N 51/00**

(22) Date of filing: **10.08.88**

This application was filed on 14 - 10 - 1991 as a divisional application to the application mentioned under INID code 60.

(30) Priority: **11.08.87 GB 8719006**

(43) Date of publication of application:
05.02.92 Bulletin 92/06

(60) Publication number of the earlier application in accordance with Art.76 EPC: **0 306 160**

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

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(54) **Molluscicides.**

(57) The use as a molluscicide of a chelate of iron (III) with a ligand of formula II

II: $[R^3NO.N=O]^-$

in which formulae:
R^3 represents:
C_1-C_6 alkyl, provided that when the alkyl group contains more than four carbon atoms the group is a branched chain alkyl group.

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This invention relates to molluscicides and in particular to slug and snail poisons.

Chemical Abstracts, vol. 101, No. 19 November 5, 1984, p233 ref No. 165584k, an abstract of JP-A-59 122405 (Moon Star Chemical Corp.) describes the use of compositions containing metal salts, to control gastropods.

Chemical Abstracts, vol. 105, No. 5 August 4, 1986 p228 ref No. 37193c, an abstract of Ann Rech. Vet. 1986, 17(1), 21-8 discloses the molluscicidal effect of iron and cuprous compounds.

It has now been found that certain iron chelates are effective molluscicides.

Accordingly the present invention comprises the use as a molluscicide of a chelate of iron (III) with a ligand of formula II

II: $[R^3NO.N=O]^-$

in which formulae:

R^3 represents:

C_1-C_6 alkyl, provided that when the alkyl group contains more than four carbon atoms the group is a branched chain alkyl group.

In general, chelates comprising three bidentate ligands, which may be identical or different, though which usually are identical, are preferred and especially those which lose one ligand molecule or ion to form a bis cation.

The ligands of formulae II are readily derived respectively from compounds of formula IIA: $R^3NOH.N=O$, by loss of a proton.

It is preferred that R^3 contains no more than four carbon atoms, R^3 is preferably methyl, ethyl or n-propyl and the chelate is preferably a trischelate of Fe^{III} comprising identical ligands.

The following compounds of formula IIA are of particular interest:

IIA: $CH_3NOH.N=O$
$CH_3CH_2NOH.N=O$
$CH_3CH_2CH_2NOH.N=O$
$(CH_3)_2CHNOH.N=O$
$CH_3(CH_3)_2CH_2NOH.N=O$
$CH_3CH_2CH(CH_3)NOH.N=O$
$(CH_3)_2CH_2CH_2NOH.N=O$

The ligands and chelates hereinbefore described may be synthesised by modification of well established routes. Synthesis of complexes comprising the ligand II may be accomplished through the following route:-

$$Mg + R^3X \longrightarrow R^3MgX$$

$$R^3MgX + NO \longrightarrow \begin{matrix} R^3\text{-}NO \\ | \\ NO \end{matrix} \diagdown\!\diagup MgX$$

$$\begin{matrix} R^3\text{-}NO \\ | \\ NO \end{matrix} \diagdown\!\diagup MgX \xrightarrow[(2)\ Fe^{3+}]{(1)\ H^+} \left[\begin{matrix} R^3\text{-}NO \\ | \\ NO \end{matrix} \right]_3 \diagdown\!\diagup Fe$$

In the foregoing formulae X represents halogen e.g. bromine or iodine.

The present chelates of the present invention may be utilised by formulation as contact poisons or in mollusc baits.

Accordingly the present invention further includes within its scope a contact poison or a poisonous bait for molluscs comprising a molluscicidal chelate hereinbefore described.

The contact poison or poisonous bait may comprise, in addition to one or more of the present molluscicidal chelates, other components, for example other molluscicids. Such components may confer

additional advantages on the contact poison or bait by, for example, synergising with th present chelates.

The present invention yet further includes with its scope a method of killing a mollusc in which th mollusc or an environment inhabited by the mollusc is treated with a molluscicidal chelate hereinbefore described.

The present chelates are of particular interest for the control of slugs because the poisons at present used, such as metaldehyde and methiocarb suffer from a disadvantage in that a proportion of the slugs in a treated population, though at first immobilised eventually recover. Environmental pollution as a result of using the chelates is, furthermore, negligible.

The present chelates also offer the advantage that they do not significantly affect ground beetles such as Carabidae beetles, which are attacked by other molluscicides e.g. methiocarb.

Suitable baits normally contain in addition to the molluscicidal chelate a carrier therefor and usually comprises a mollusc food such as a cereal e.g. wheatmeal, comminuted cuttle fish, starch or gelatin, which may also serve as a carrier. A mollusc phagostimulant such as a sugar e.g. sucrose, or molasses is usually included. Non nutrient carriers of interest include non nutrient polymeric materials, pumice, carbon and materials useful as carriers for insecticides. The bait usually comprises a binder, which is suitably waterproof, such as paraffin wax or casein and may advantageously comprise a bird repellent, for example a blue colourant. In order to inhibit deterioration of the bait a fungistat may be included.

Typically the bait contains at least 3% by weight and no more than 16% by weight of molluscicide. The preferred concentration in the bait is generally 10-13% by weight.

When used as a contact poison the molluscide is typically formulated as a dust or spray, for application to foliage, soil, stubble or trash (plant residues). Examples of solid carriers include talc, chalk bentonite, clay and the like and examples of liquid carriers include water (if necessary with an emulsifier), alcohols e.g. lower alcohols such as methanol or ethanol, ketones e.g. lower ketones such as acetone or methyl ethyl ketone, liquid hydrocarbons and the like.

The treatment of both terrestrial and aquatic molluscs in accordance with the present invention is envisaged, the species Deroceras reticulatum, Arion hortensis, Milax budapestensis, Cepaea hortensis, Helix aspersa and Achatina spp being of particular interest as targets.

The invention is illustrated by the following Examples:

Examples 1-8

Bioassay Method

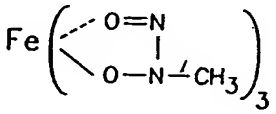
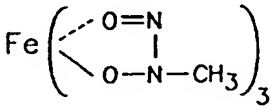
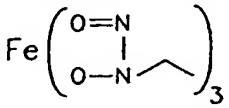
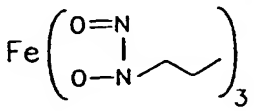
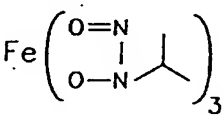
Test compounds were incorporated into a standard wheat-flour-based edible carrier containing 10% paraffin wax binder and 2.5% sucrose phagostimulant, in increasing concentrations 0, 1, 4, 7, 10, 13 and 16% a.i.

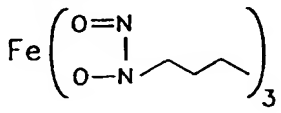
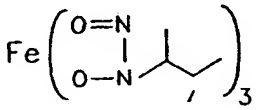
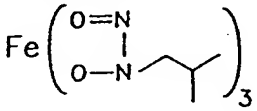
Groups of ten field-collected D. reticulatum in the weight range 400-600 mg were confined with 0.5 g DM test bait at each concentration for a period of 4 days under a regime of 12 h dark @ 5° C and 12 light @ 15° C. Weight of bait eaten and number of slugs killed were recorded.

The results are shown in Table I. Where six groups of ten slugs are offered bait containing 1,4,7,10,13 or 16% a.i., the results have been reduced to two values, (i), the total amount of a.i. ingested (mg) which gives an indication of the palatability of the compound, and (ii), the total number of slugs killed (x/60) which, with (i), gives an indication of its relative toxicity with metaldehyde and methiocarb under field conditions (grass/clover).

TABLE I

Effect of increasing concentrations of iron and aluminium chelates in a standard bait on feeding and kill of Deroceras reticulatum

Example	Compound	a.i. (%)	Eaten (%)	Kill (x/60)
1	Tris (N-nitroso-N-methyl hydroxylaminato) Fe III 		100 17 11 4 8 5 7	2 5 8 5 5 7 8
2	Tris (N-nitroso-N-methyl hydroxylaminato) Fe III 	17	38	
3	Tris (N-nitroso-N-ethyl hydroxylaminato) Fe III 	6	49	
4	Tris (N-nitroso-N-n-propyl hydroxylaminato) Fe III 	50 55	58 58	
5	Tris (N-nitroso-N-2-propyl hydroxylaminato) Fe III 	3	43	

Example	Compound	a.i.ingested (mg/60 slugs)	Slugs dead (x/10)
6	Tris (N-nitroso-N-n-butyl hydroxylaminato) Fe III 	53	37
7	Tris (N-nitroso-N-2-butyl hydroxylaminato) Fe III 	54	46
8	Tris (N-nitroso-N-2-methylpropyl hydroxylaminato) Fe III 	160	42

Claims

1. The use as a molluscicide of a chelate of iron (III) with a ligand of formula II

   II: $[R^3NO.N=O]^-$

   in which formulae:
   R^3 represents:
   C_1-C_6 alkyl, provided that when the alkyl group contains more than four carbon atoms the group is a branched chain alkyl group.

2. A use according to Claim 1, in which the chelate comprises three identical bidentate ligands.

3. A use according to Claim 2, in which R^3 contains no more than four carbon atoms.

4. A use according to Claim 3, in which R^3 is methyl, ethyl, or n-propyl.

5. A use according to Claim 3, in which the chelate comprises a ligand formed by loss of a proton from one of the following compounds:

   $CH_3NOH.N=O$
   $CH_3CH_2NOH.N=O$
   $CH_3CH_2CH_2NOH.N=O$
   $(CH_3)_2CHNOH.N=O$
   $CH_3(CH_3)_2CH_2NOH.N=O$
   $CH_3CH_2CH(CH_3)NOH.N=O$
   $(CH_3)_2CH_2CH_2NOH.N=O$

6. A use according to Claim 3, in which th chelate is of formula: $Fe^{III}[CH_3NON=O)_3$ or Fe^{III}-$[CH_3CH_2NON=O]_3$ or $Fe^{III}[CH_3CH_2CH_2NON=O]_3$.

7. A contact poison or poisonous bait for molluscs, comprising a molluscicidal chelat as hereinbefore defined.

8. A poison bait for molluscs according to Claim 7, which comprises a chelate molluscicide as hereinbefore defined and a carrier therefor.

9. A poison bait according to Claim 7 or 8, which comprises a mollusc food.

10. A poison bait according to Claim 9, in which the mollusc food is a cereal, comminuted cuttle fish, mollases or gelatin.

11. A poison bait according to any of Claims 7 to 10 which comprises a mollusc phagostimulant.

12. A poison bait according to Claim 11, in which the phagostimulant is a sugar or starch.

13. A poison bait according to Claims 7 or 8 which comprises a non nutrient carrier.

14. A poison bait according to Claim 13, in which the non nutrient carrier is an artificial polymer, pumice, carbon or a material useful as a carrier for an insecticide.

15. A poison bait according to any of Claims 7 to 14, which comprises a binder.

16. A poison bait according to Claim 15, in which the binder is paraffin wax or casein.

17. A poison bait according to any of Claims 7 to 16, which comprises a bird repellent.

18. A poison bait according to Claim 17, in which the bird repellent is a blue colourant.

19. A poison bait according to any of Claims 7 to 18, which comprises a fungistat.

20. A poison bait according to any of Claims 7 to 19, which comprises at least 3% by weight of a molluscicidal chelate as hereinbefore defined.

21. A poison bait according to any of Claims 7 to 20, which comprises no more than 16% by weight of a molluscicidal chelate as hereinbefore defined.

22. A poison bait according to any of Claims 7 to 21, which comprises 10 - 12% by weight of a molluscicidal chelate as hereinbefore defined.

23. A process for the production of a poison bait for molluscs in which a chelate molluscicide as hereinbefore defined is formulated with a carrier therefor.

24. A method of killing a mollusc in which the mollusc or an environment inhabited by the mollusc is treated with a molluscicidal chelate hereinbefore defined.

25. A method according to Claim 24, in which an environment inhabited by the mollusc is treated with a poison bait comprising a chelate hereinbefore defined.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 20 2673

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A,D	CHEMICAL ABSTRACTS, vol. 101, no. 19, 5th November 1984, page 233, abstract no. 165584k, Columbus, Ohio, US; & JP-A-59 122 405 (MOON-STAR CHEMICAL CORP.) 14-07-1984 * Abstract *	1-25	A 01 N 51/00
A,D	CHEMICAL ABSTRACTS, vol. 105, no. 5, 4th August 1986, page 228, abstract no. 37193c, Columbus, Columbus, Ohio, US; M. VINCENT et al.: "Effects of two metal salts (iron(III) chloride, copper(II) chloride) on predation and oviposition by Zonitoides nitidus Mueller (Mollusca, Gastropoda, pulmonata)", & ANN. RECH. VET. 1986, 17(1), 21-8 * Abstract *	1-25	
A	FR-A-1 188 542 (BASF) * Page 1, left-hand column *	1-25	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A 01 N

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	20 Nov mber 91	DECORTE D.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document